ones, A (49%) and B (34%), had similar short retention times while the minor constituents, C (9.5%) and D (7.3%), had longer but similar retention times. Comparisons with samples obtained in the reduction of vinylcyclohexanol indicated that B was ethylidenecyclohexane and C was vinylcyclohexene. The two major components were not resolved on a preparative Carbowax column, but a sample of a mixture of the two, n^{20}_{D} 1.4588, could be obtained. The infrared spectrum contained the bands shown by ethylcyclohexene (API No. 1958) (lit.[39] n^{20}_{D} 1.4576) and by ethylidenecyclohexane (API No. 1962), n^{20}_{D} 1.4260.

Hydrogenolysis of Pulegone.—Pulegone, as purified on a Carbowax 20 M preparative column at 150°, had n^{19}_{D} 1.4878 (lit.[40] n^{19}_{D} 1.4880) and α^{20}_{D} $+20.87°$ (neat, 1 dcm.) (lit.[41] $[\alpha]^{15}_{\text{D}}$ $+23.60°$). Reduction of 2.0 g. (13 mmoles) with 50 ml. (50 mmoles) of 3:1 reagent for 4 hr. at room temperature gave a crude product, containing (by v.p.c.) 83% of hydrocarbon, 7% of menthone and isomenthone, and four components of higher retention time which may be alcohols. The hydrocarbon distillate (1.20 g., 71%) was analyzed and fractionated on a Carbowax 20 M column to give four products which were identified by their refractive indices, optical rotations, and infrared spectra[42,43]: 3-menthene (41%), n^{20}_{D} 1.4522, $[\alpha]^{20}_{\text{D}}$ $+112°$ (*c* 1.00, chloroform) (lit.[42] n^{20}_{D} 1.4519, lit.[44] 1.4523, lit.[44] $[\alpha]^{20}_{\text{D}}$ 114.5°, homogeneous); 4(8)-menthene (35%), n^{20}_{D} 1.4682, optically inactive (lit.[42] n^{20}_{D} 1.4689); 3,8-menthadiene (13%), n^{20}_{D} 1.4930, $[\alpha]^{20}_{\text{D}}$ $+159°$ (*c* 0.898 chloroform) (lit.[43] n^{20}_{D} 1.4936, lit.[12] 1.4893, lit.[41] $[\alpha]^{14}_{\text{D}}$ $+140.6°$); 2,4(8)-menthadiene (12%), n^{20}_{D} 1.5037, $[\alpha]^{20}_{\text{D}}$ $+63°$, (*c* 0.312, chloroform) (lit.[43] n^{20}_{D} 1.5050, lit.[12] 1.5030).

Hydrogenolyses of Linalool, Nerol, and Geraniol.—Commercial linalool (Eastman Kodak, white label) was found to be about 98% pure by v.p.c. on Carbowax 20 M at 130° and was used directly. The alcohol (3.08 g., 20 mmoles) was added dropwise over a 10-min. period to 80 ml. (80 mmoles) of "dichloroaluminum hydride" cooled in an ice bath. The solution was let stand 5 hr. at room temperature and then poured on ice and worked up in the usual way. Flash distillation under vacuum gave 2.26 g. (*ca.* 81%) of hydrocarbon mixture; this mixture was analyzed by v.p.c. on Carbowax 20 M and oxyadiponitrile–silver nitrate (see Table I). Commercial nerol (Fluka), found to contain 39% of geraniol by v.p.c., gave 2.15 g. (77%) of hydrocarbon mixture in a fully parallel experiment.

A sample of pure nerol, n^{20}_{D} 1.4748 (lit.[45] n_{D} 1.4754), was obtained by repetitive gas chromatography at 160° on a Carbowax 20 M analytical column; this product gave a single peak on v.p.c. analysis. Practical grade geraniol (Eastman Kodak) was partially purified by conversion to the crystalline calcium chloride complex[46] and then further purified by v.p.c. on Carbowax 20 M at 180° to give a product with n^{20}_{D} 1.4777 (lit.[47] n^{20}_{D} 1.4766). These two alcohols were separately reduced in parallel runs; 30 mg. (0.2 mmole) of alcohol was added to 0.80 ml. (0.8 mmole) of "dichloroaluminum hydride" in ice-chilled screwcap vials. The vials were closed and held at room temperature for 5 hr. Then several drops of water were added and the ether solutions were transferred to separate vials and dried over potassium carbonate and then sodium sulfate. These mixtures were analyzed by v.p.c. without concentration (see Table I). Assuming 100% material balance in the analysis, it was found that about 10% of alcohol had not reacted in each case; the residual alcohol was, in each case, apparently pure starting material. Infrared spectra were obtained for all substances for which refractive indices are reported; they were identical with those of authentic samples or comparable to published ones.

Commercial citral was fractionated by v.p.c. on Carbowax 20 M at 125°[48] to give a sample of neral, n^{22}_{D} 1.4852 (lit.[49] n^{20}_{D} 1.4869). This substance gave a mixture virtually identical with that obtained from nerol on hydrogenolysis with 3:1 reagent.

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Hydrogenolyses with Chloroaluminum Hydrides. IV. Saturated and Homobenzylic Alcohols[1]

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Saturated alcohols react with "dichloroaluminum hydride" at 60–80° in higher-boiling ethers to give hydrocarbons. Wholly aliphatic secondary and tertiary alcohols give some reduction but large amounts of olefins are formed. β-Phenyl alcohols give predominating reduction of the hydroxy group. Rearrangements suggestive of carbonium ion processes are observed in several instances.

Evidence indicating that hydrogenolyses with mixtures of aluminum chloride and lithium aluminum hydride occur with the formation of carbonium ions[2-5] suggested the possibility that conditions might be found for the hydrogenolysis of saturated alcohols. Orientation experiments (in which the products were analyzed by gas chromatography, but in which individual products were not actually isolated) indicated that saturated secondary and tertiary alcohols do indeed react with "dichloroaluminum hydride"[3-5] in di-*n*-butyl ether or in diphenyl ether at 60–80° to give small amounts of paraffins together with large amounts of olefins. Phenyl-2-propanone gave nearly pure *n*-propylbenzene while benzyldimethylcarbinol gave nearly equal amounts of isobutylbenzene and a mixture of olefins. No hydrocarbons were, however, obtained from 1-hexanol, which was recovered on hydrolysis of the reaction mixture.

In experiments in which pure products were isolated and identified by comparisons of infrared spectra with authentic samples, several other homobenzylic alcohols gave principally products of reduction rather than of elimination. Thus, *trans*-2-phenylcyclopentanol gave phenylcyclopentane containing about 11% of 1-phenylcyclopentene, while 2-phenylcyclohexanol (mixed isomers) gave a 1:2:1 mixture of benzylcyclopentane, phenylcyclohexane, and 1-phenylcyclohexene. Reduction of 1,1-diphenyl-2-propanone, or of the corresponding alcohol, gave 1,2-diphenylpropane.

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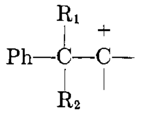
The failure of 1-hexanol to undergo reduction, elimination, or conversion to chloride suggests strongly that the transition state for each of these reactions has a high degree of carbonium ion character. The formation of olefins[4,5] as by-products (or even major products as above) and of chloride,[4] the occurrence of alkylation of olefins[3,5] and aromatics,[4] and the isomerizations mentioned earlier are all accounted for most easily by the postulate that a carbonium ion intermediate is formed. The rearrangements observed here in the homobenzylic systems can all be interpreted as involving rearrangement of the initial carbonium ion (I) to a benzylic carbonium ion (II) by 1,2-migration of a hydrogen atom, an alkyl group, or an aromatic group. On this basis, we suggest that the formation of 1-phenylcyclopentene from *trans*-2-phenylcyclopentanol occurs by way of loss of a proton from the rearranged tertiary phenylcyclopentyl carbonium ion (IV) rather than by *cis* elimination.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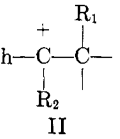
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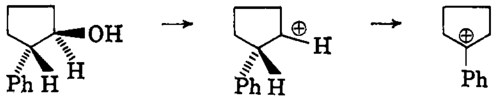

III IV

Experimental

Vapor phase chromatographic (v.p.c.) analyses and separations were performed with an Aerograph Model A-90-C using silicone or Carbowax analytical columns or a Craig polyadipate preparative column. Identifications by retention time were based on successive alternating runs of mixtures and authentic samples of pure hydrocarbons, many of which were provided by Prof. H. C. Brown. Identification by infrared spectra was based on comparisons with published data or with spectra of authentic samples of hydrocarbons prepared by literature methods and purified by preparative gas chromatography.

Orientation Experiments.—The following compounds, 1-hexanol, 2-octanol, cyclohexanol, cyclopentanone, 1-methylcyclohexanol, triethylcarbinol, phenyl-2-propanone, and benzyldimethylcarbinol, were subjected to reaction conditions described subsequently, the major variation being one of scale of operations. Hydrocarbons were obtained in amounts corresponding to 60–90% yields, except from 1-hexanol, which gave no hydrocarbon. In these experiments the products were analyzed by v.p.c. without isolation of individual components.

In an apparatus that could be set for distillation or reflux was placed a mixture of 20.8 g. (0.16 mole) of aluminum chloride, 50 ml. of 1 *M* lithium aluminum hydride (0.05 mole) in diethyl ether, and 60 ml. of diphenyl ether or di-*n*-butyl ether. About 0.05 mole of the alcohol or ketone was added and diethyl ether was distilled (Dry Ice cooled receiver) until the internal temperature was at about the boiling point of the expected hydrocarbon or 80°, whichever was lower. The mixture was heated at reflux for 3 hr., and the products were obtained either by further distillation or by decomposition of the mixture on ice and extraction with ether. Ethereal distillates and extracts were combined and distilled to remove most of the ether before v.p.c. analysis. Each of the saturated secondary alcohols gave products containing 10% of paraffin and 90% of olefin; the hydrocarbon from 2-octanol contained about 10% of 1-octene and 80% of a mixture of the 2-octenes. The hydrocarbon from methylcyclohexanol appeared to be about 50% methylcyclohexane and 50% 1-methylcyclohexene, while that from triethylcarbinol appeared to be pure 3-ethyl-2-pentane. The hydrocarbon from phenyl-2-propanone appeared to be essentially pure *n*-propylbenzene, while that from benzyldimethylcarbinol appeared to be 50% isobutylbenzene and 50% of a mixture of phenyl-2-methylpropenes.

Hydrogenolysis of 2-Phenylcyclohexanol.—Commercial 2-phenylcyclohexanol (both isomers) (10 g., 0.059 mole) was added to a solution of 3 g. (0.081 mole) of lithium aluminum hydride and 21 g. (0.16 mole) of aluminum chloride in 75 ml. of di-*n*-butyl ether, and the mixture was heated at 80° for 8 hr. The mixture was cooled and decomposed on ice, and the organic layer was separated, dried, and distilled at 102–118° (2 mm.) to give 6 g. of mixed hydrocarbons. Repeated gas chromatography on a preparative Craig polyadipate column gave four fractions. The first fraction was small and could not be identified. The second (about 25% of the hydrocarbon) had n^{20}_{D} 1.5180 and gave an infrared spectrum corresponding to that of benzylcyclopentane[6] (lit.[6] n^{20}_{D} 1.5178). The third fraction (about 50%) had n^{20}_{D} 1.5259 and gave an infrared spectrum corresponding to that of phenylcyclohexane[6] (lit.[6] n^{20}_{D} 1.5255). The fourth fraction (about 25%) had n^{20}_{D} 1.5675 and gave an infrared spectrum corresponding to that of 1-phenylcyclohexene[6] (lit.[6] n^{20}_{D} 1.5692).

1,1-Diphenyl-2-propanone, m.p. 45.5–47° (lit.[7] m.p. 46°), was prepared by dehydration of 1,2-dihydroxy-1,1-diphenylpropane with dilute sulfuric acid,[8] the diol having been prepared by the reaction of phenylmagnesium bromide with ethyl lactate.[8]

1,1-Diphenylpropane was prepared by the Huang-Minlon modification of the Wolff–Kishner reduction[9] of 1,1-diphenyl-2-propanone. The product was fractionated on a polyester product column to give a 57% yield of 1,1-diphenylpropane, n^{21}_{D} 1.5634 (lit.[10] n^{20}_{D} 1.5643), infrared spectrum identical with one reported earlier,[11] and also 27% of diphenylmethane, n^{21}_{D} 1.5766 (lit.[12] n^{20}_{D} 1.5768), m.p. 25–27° (lit.[12] m.p. 26–27°), infrared spectrum identical with that of an authentic sample.

Hydrogenolysis of 1,1-Diphenyl-2-propanone and 1,1-Diphenyl-2-propanol.—A mixture, prepared by adding 2.10 g. (10 mmoles) of 1,1-diphenyl-2-propanone to mixed hydride reagent from 3.7 g. (28 mmoles) of anhydrous aluminum chloride and 10 ml. of 1 *M* ethereal lithium aluminum hydride, was heated at 75° until no further ether distilled. Heating was continued at 68° for 4.5 days and worked up in the usual way to give 1.73 g. (88%) of 1,2-diphenylpropane, b.p. 87–88° (2 mm.), n^{21}_{D} 1.5585 (lit.[10] n^{20}_{D} 1.5585). The infrared spectrum was superimposable on that of an authentic sample (part I, this series[3]) and different from that of 1,1-diphenylpropane. The presence of small amounts of the latter hydrocarbon is not excluded, however, since no v.p.c. separation of the isomeric hydrocarbons could be achieved on the columns available to us.

In a separate run the same amounts of materials were not heated but held at room temperature for 1 hr. Work-up in the usual manner gave almost pure 1,1-diphenyl-2-propanol, m.p. 63.5–64.5° (lit.[13] m.p. 63–64°). Hydrogenolysis of this carbinol under conditions used for the ketone gave, after fractionation of the product on a preparative v.p.c. column, 61% of 1,2-diphenylpropane, n^{21}_{D} 1.5582, indistinguishable by v.p.c. or infrared spectroscopy from that obtained from the ketone.

Under the reaction conditions described above, 1,1,1-triphenyl-2-propanol[14] gave an insoluble white substance, from which, on hydrolysis, 71% of the starting material was recovered.

***trans*-2-Phenylcyclopentanol,** b.p. 112–117° (1 mm.), n^{21}_{D} 1.5478, phenylurethane, m.p. 81–82.5° [lit.[15] b.p. 110–113° (2 mm.), n^{25}_{D} 1.5478, phenylurethane, m.p. 82–83°] was prepared[16] by hydroboration[17] of 1-phenylcyclopentene.[18]

***trans*-2-Phenylcyclopentyl tosylate** was prepared by the general method of Brown and Ham[19]; on a 0.185 *M* scale yields of 80% of the tosylate, m.p. 66–67° (hexane), were obtained. The analytical sample had m.p. 68–69°.

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Anal. Calcd. for $C_{18}H_{20}SO_3$: C, 68.32; H, 6.37. Found: C, 68.20; H, 6.42.

3-Phenylcyclopentene.—A solution of sodium ethoxide prepared from 7 g. (0.3 g.-atom) of sodium and 500 ml. of absolute ethanol was heated to 80° under nitrogen. A solution of 31.2 g. (0.099 mole) of *trans*-2-phenylcyclopentyl tosylate in 500 ml. of absolute ethanol was added dropwise over 46 hr. The mixture was heated for 7 hr., cooled to room temperature, diluted with water, and extracted three times with petroleum ether (b.p. 35–37°). The extract was dried, concentrated, and distilled through a 12-in. spiral-packed rectifying column to give 5.5 g. (38.5%) of 3-phenylcyclopentene, b.p. 51.5–54° (1 mm.), $n^{20.6}_{\mathrm{D}}$ 1.5415 [lit.[20] b.p. 92–93° (13 mm.), n^{19}_{D} 1.5396]. This olefin is readily separated from the higher boiling 1-phenylcyclopentene by vacuum distillation or, for analytical purposes, by gas chromatography.

Phenylcyclopentane was prepared by catalytic hydrogenation of 1-phenylcyclopentene over platinum in methanol; b.p. 49–53° (1 mm.), n^{20}_{D} 1.5283 (lit.[21] b.p. 213–215°, n_{D} 1.5320). This substance had the same retention time as 3-phenylcyclopentene on silicone or Carbowax gas chromatography columns; its infrared spectrum lacked a number of moderately strong peaks shown by that of the 3-olefin.

Hydrogenolysis of *trans*-2-Phenylcyclopentanol.—In a flask fitted with an addition funnel, a magnetic stirrer, and a distilling head was placed 3.6 g. (0.0224 mole) of *trans*-2-phenylcyclopentanol. The system was flushed with nitrogen and 75 ml. of a 1.22 *N* hydride solution, prepared from 8.5 g. (0.224 mole) of lithium aluminum hydride and 180 g. (0.6 mole) of crystalline aluminum chloride in 800 ml. of ether, was added dropwise with stirring. The flask was then heated, distilling ether until the internal temperature reached 70°, which temperature was maintained for 24 hr. The mixture was cooled, diluted with ether, treated cautiously with water, and extracted with ether. Concentration gave 3.2 g. of a yellow oil which was distilled under vacuum. The distillate, b.p. 55–64° (1 mm.), amounted to 1.58 g., $n^{19.5}_{\mathrm{D}}$ 1.5364, and gave an infrared spectrum indicating it to be slightly impure phenylcyclopentane. Analysis by v.p.c. showed two peaks, the first (89% of the total area) corresponding to phenylcyclopentane and the second (11% of the total area) to 1-phenylcyclopentene. The refractive index of the product is that to be expected of a mixture of 88% phenylcyclopentane and 12% 1-phenylcyclopentene, indicating that little or none of the 3-olefin is present.

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Dehydration of Alcohols, Diols, and Related Compounds in Dimethyl Sulfoxide[1]

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This report lists additional examples of the dehydration of alcohols (particularly 1-alkylcycloalkanols) to olefins, the dehydration of alcohols to ethers and certain diols to cyclic ethers, the pinacol rearrangement *vs.* diene formation from 1,2-diols, the dehydration and in part oxidation of two 1,3-diols, the conversion of ethers to olefins, and the preparation of furans from 1,4-diketones. Additional observations on the mechanism are discussed.

The initial report of the dehydration of alcohols in dimethyl sulfoxide described the scope of the reaction as limited to secondary and tertiary benzylic alcohols and tertiary aliphatic alcohols.[3] In view of the stereochemistry of the elimination in *erythro*- and *threo*-1,2-diphenyl-1-propanol and other data, the mechanism of this dehydration appeared to involve carbonium ions.[3] In this paper we wish to extend the scope of this reaction and offer additional comments about the mechanism.

The previous paper in this series noted several examples of primary and secondary alcohols which failed to dehydrate[3]; among these was 1-phenyl-2-propanol. However, when this alcohol was heated in dimethyl sulfoxide at 190° for 48 hr. under nitrogen, 41% of 1-phenylpropene, 49% of unchanged alcohol, and less than 1% of phenylacetone were found. Performing the reaction in air caused the formation of appreciable amounts of phenylacetone (25%). This example represents the first successful dehydration of a simple secondary alcohol in dimethyl sulfoxide. Additional cases of dehydration of primary and secondary alcohols in polyfunctional compounds will appear later.

The newest group of tertiary alcohols capable of dehydration in dimethyl sulfoxide are the 1-alkylcycloalkanols, and data concerning these examples are listed in Table I. Analysis of the olefin composition was by v.p.c. while identification of these products employed various combinations of physical constants, infrared spectra, and/or n.m.r. spectra. The major product in each of these reactions was the endocyclic olefin, 1-alkylcycloalkene. In the case of 1-methylcyclohexanol, dehydration in dimethyl sulfoxide produced an olefin mixture (1-methylcyclohexene and methylenecyclohexane) similar with that obtained from an iodine- or *p*-toluenesulfonic acid[4]-catalyzed dehydration. The result remains consistent with a carbonium ion intermediate in the dimethyl sulfoxide dehydration. The appearance of 2-cyclohexylpropene from 1-isopropylcyclohexanol requires double bond migration which can be accommodated by intermediate carbonium ions.

The dehydration of 1,2-diphenylethanol in dimethyl sulfoxide produced *trans*-stilbene (93%) and unchanged alcohol (5%).

When a series of experiments was performed on the dehydration of 1-phenyl-1-propanol in varying amounts of dimethylsulfoxide, a new mode of dehydration was observed, namely, ether formation. These data are summarized in Table II and show that, in the presence of small amounts of dimethyl sulfoxide, ether production is favored. Control experiments ruled out a thermal

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[1] Acknowledgment is made to the donors of the Petroleum Research Fund administered by the American Chemical Society for support of this research.

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